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Quarterly Technical Summary Report No. 11

December 1, 1964 to February 28, 1965

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RESEARCH ON THE DEFLAGRATION OF
HIGH-ENERGY SOLID OXIDIZERS (U)

Contract No. AF 49(638)-1169

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JUL 9 1965

to

Air Force Office of Scientific Research
Washington 25, D. C.

from

Kinetics and Combustion Group
Atlantic Research Corporation
Alexandria, Virginia

May 19, 1965

Chief Investigators: J. B. Levy

Internal Consultants: G. von Elbe and R. Friedman

Chemist: S. J. Adams

Chemist: E. T. McHale

Chemist: C. Midkiff

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RESEARCH ON THE DEFLAGRATION OF HIGH-ENERGY SOLID OXIDIZERS (U)

I. ABSTRACT

Further experiments have been performed in which the flame temperature above deflagrating hydrazine diperchlorate has been measured with fine thermocouples. Results have been obtained with ceramic-coated Pt-Pt, 10% Rh thermocouples and with uncoated chromel-alumel thermocouples. A flame temperature of about 1350°K is indicated for an ambient pressure of about 20 atmospheres. This is substantially below the theoretical flame temperature of about 1600°K.

The thermal decomposition of hydrazine diperchlorate has been investigated from 211-291°C. Ammonium perchlorate, nitrogen, oxygen, hydrogen chloride, nitrous oxide and hydrogen have been identified as products and qualitative evidence of the formation of perchloric acid has also been obtained. Quantitative analysis of the products has allowed a stoichiometric equation to be written. The rates of thermal decomposition have been examined and indicate a complex process. Preliminary experiments have been performed on the thermal decomposition of hydrazine diperchlorate-copper chromite mixtures. Ammonium perchlorate has been found in the surface of a strand of hydrazine diperchlorate which had been ignited at an elevated pressure, allowed to deflagrate partially and extinguished by sudden pressure release.

Deflagration rate measurements from six to one hundred and thirty atmospheres are reported for pressed hydrazine diperchlorate.

II. INTRODUCTION

In this program we are studying the deflagration of a series of high-energy oxidizers. Our studies on hydrazine perchlorate have recently been reported (1). More recently we have been investigating hydrazine diperchlorate.* We are pursuing the following lines of research: the self-deflagration of hydrazine diperchlorate in inert gas at elevated pressures; the effects of catalysts on deflagration rate; the measurement of the flame temperature above a strand of deflagrating

* This will be denoted here by the abbreviation HDP.

hydrazine diperchlorate; the thermal decomposition of hydrazine diperchlorate, both pure and catalyzed.

III. PROGRESS DURING PRESENT PERIOD

During the present period we have performed experiments in which (a) flame temperatures of deflagrating HDP were measured, (b) thermal decomposition studies on HDP and HDP-copper-chromite mixtures were performed, and (c) deflagration rates of HDP over a wide pressure range were determined. These are discussed below.

A. The Flame Temperature of Hydrazine Diperchlorate

Attempts continued during the past quarter to measure the flame temperature of hydrazine diperchlorate by means of fine thermocouples. As previously reported (2), Pt - Pt/10% Rh thermocouples imbedded in pressed strands were observed to catalyze a subsurface reaction. To overcome this difficulty, the thermocouples were coated with NBS A-418 Ceramic Coating. Such a technique has been reported to be very satisfactory (3).

Thermocouples made of 2 mil and 1 mil wire were used. The thermocouple beads, after coating, averaged 12.5 mil in diameter for the 2 mil wire, and 4.5 mil in diameter for the 1 mil wire. Both size thermocouples required large corrections for radiation heat loss. Motion pictures were taken of the deflagration of the strands containing the coated thermocouples and showed no evidence of any catalytic activity.

Rather erratic results were obtained with these thermocouples, and this is attributed to the method of mounting the strands and to the quality control of the hydrazine diperchlorate. The strands were mounted into loose-fitting Pyrex tubes with slits cut down the sides. This allowed the thermocouple wires to pass through the glass and through a hole drilled laterally through the strand. Motion pictures showed that the strands burned very erratically in this mounting, and the temperature profiles obtained on the Visicorder bore no resemblance to a theoretical temperature profile through a burning solid surface. When tight-fitting tubes were used and holes were drilled through the glass and strands to accommodate the thermocouples, the burning of the strands

took place with uniform regression of the surface and the temperature profiles showed marked improvement. However, the temperatures measured were still erratic. This was strongly suspected as being due to different batches of hydrazine diperchlorate exhibiting different flame temperatures.

Subsequently, the coated platinum couples were abandoned in favor of uncoated Chromel-Alumel* thermocouples, when the latter were discovered not to give rise to any catalysis and not to melt in the flame. Furthermore, much more careful attention was given to the quality control of the hydrazine diperchlorate. The latest measurements of the flame temperature seemed to show much improved consistency. However, further data could not be obtained because the supply of hydrazine diperchlorate was exhausted. More experiments are planned.

In Table I are given the data obtained to date. All runs were made at pressures of 300 to 400 psig of flowing nitrogen. The observed temperatures are lower than the true gas temperature because of radiation loss of the thermocouples. The corrections to be applied were calculated using the formula,

$$T_g - T_c = \frac{\epsilon \sigma d (T_c^4 - T_w^4)}{\lambda \text{ Nu}}$$

where T_g = true gas temperature

T_c = thermocouple temperature observed

T_w = temperature of surface absorbing radiation

σ = Stefan-Boltzmann constant

ϵ = emissivity of thermocouple

d = bead diameter

λ = thermal conductivity coefficient of gas

Nu = Nusselt number

The emissivity of the VES Ceramic Coating is given as 0.87 (4); the emissivity of Ch-Al is 0.36 for the unoxidized metal and 0.87 for the oxidized (5); λ was calculated by the method of Andrussow (6) using the theoretical gas composition; the Nusselt number was obtained from the Reynolds number (7).

* Designated hereafter by Ch-Al.

TABLE I

Flame Temperature Measurements for Hydrazine
Diperchlorate Using Fine Thermocouples

<u>Run</u>	<u>T observed ($^{\circ}$K)</u>	<u>Radiation Correction ($^{\circ}$K)</u>	<u>Remarks</u>
1	1460	195	12.5 mil ceramic-coated Pt couple; loose-fitting mounting tube with slit.
2	1380	195	"
3	1450	105	4.5 mil ceramic-coated Pt couple; loose-fitting mounting tube with slit.
4	1405	105	"
5	1405	105	"
6	1480	105	"
7	1290	105	"
8	1480	105	"
9	1325	195	12.5 mil ceramic-coated Pt couple; tight-fitting mounting tube with hole drilled.
10	1355	195	"
11	1225	105	Same but 4.5 mil couple
12	1180	105	"
13	1425	24-58	2.5 mil uncoated Ch-Al couple; tight-fitting mounting tube with hole drilled
14	1325	24-58	"
15	1525	"	"
16	1355	"	"
17	1355	"	"
18	1325	"	"
19	1370	"	"

The Ch-Al thermocouple measurements yield fairly constant flame temperatures, significantly below the theoretical value of 1600°K. It appears that thermodynamic equilibrium is not attained and that the chemical reaction in the terminal stage of the deflagration process tends to "freeze" at random temperature levels.

Examination of the temperature profiles obtained on the Visicorder for the runs using Ch-Al thermocouples shows that the thickness of the heated solid zone of hydrazine dperchlorate is of the order of 0.4 mm at 21 atmospheres. This must be regarded as a preliminary measurement, but it can be compared with the thickness of the condensed phase reaction zone for hydrazine perchlorate (containing 5% Del-Rin and 0.5% MgO). The latter is reported (8) to be 0.5 mm at 0.5 atm and 0.3 mm at 21 atm. It may be noted that the deflagration rate of hydrazine dperchlorate at 300 psig is comparable to that of the hydrazine perchlorate at 0.5 to 1 atm.

B. Thermal Decomposition Studies

1. Product Analyses

We have performed a number of experiments in which we have decomposed HDP thermally and followed the rate of gas evolution manometrically or have examined the solid after various periods of heating to see if ammonium perchlorate or hydrazine perchlorate could be detected there.

The experiments have been performed by means of a vacuum line. The amounts of HDP used have been of the order of 50 mg. The sample has been heated in a small 7 mm o.d. reaction tube which has been inserted in a well in an electrically-heated block. The temperature was maintained constant to $\pm 1^\circ\text{C}$ manually.

Experiments with pure HDP have been performed at temperatures from 174°C to 293°C. The residues were examined for the presence of AP, HP and HDP by infrared spectroscopy. Residues were removed from the reaction tube at the conclusion of an experiment and ground with Kel-F-3 oil to form a mull. The resulting mull was placed between two rock salt blocks and the infrared spectrum was taken.

The peaks used to identify the components are tabulated in Table II.

TABLE II
Infrared Absorption Peaks

Substance	Frequency in Wave Numbers
Hydrazine Diperchlorate	2720, 2645, 2570, 1480
Hydrazine Perchlorate	3250, 1593, 1523
Ammonium Perchlorate	1420

The rates of decomposition were such that useful experiments could be performed from 211-291°C. The product analysis results are shown in Table III.

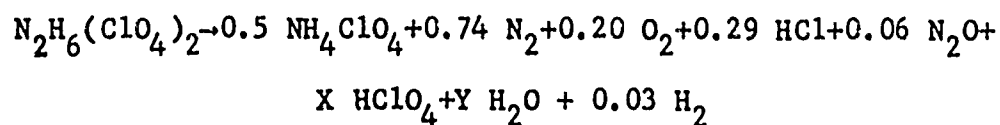
TABLE III
Products of the Thermal Decomposition of
Hydrazine Diperchlorate

No.	Expt.	Weight of HDP (g)	Temp. (°C)	Time Heated (minutes)	Present in Solid Residue	Mole/mole HDP Charged
1	E-243	0.015	280	2	AP	-
2	E-244	0.020	280	7	AP	-
3	E-253	0.078	211	109	AP,HP	-
4	E-254	0.070	212	365	HP,HDP,AP	-
5	E-257	0.028	292	83.5	AP	0.65
6	E-258	0.035	291	38	AP	0.60
7	E-259	0.031	293	24	AP	0.50

For all of these experiments droplets of an acidic liquid were observed to form on the tube walls above the metal block. It is believed that this is aqueous perchloric acid.

For table entry No. 7, the gases evolved were analyzed by means of the mass spectrograph and nitrogen, hydrogen, water, oxygen, nitrous oxide and hydrogen chloride were found.

The quantitative analysis leads to the equation



If $X = 1.2$ and $Y = 0.7$, the mass balance is as shown below:

Atoms	HDP	Products
N	2.0	2.1
H	6.0	5.1
O	8.0	8.0
Cl	2.0	2.0

With the exception of hydrogen the agreement is excellent.

2. The Rate of Thermal Decomposition

Pressure-time curves for four runs are shown in Figure 1. Three of these runs are at $292 \pm 1^\circ\text{C}$ (entries 257, 258 and 259) while one is at 212°C (entry 254). The curves are not regular or reproducible but they do have similarities. They all show a steep initial rise followed by a slower increase. The curves for entries 259 and 258 showed a sudden increase to the final pressure while that for 257 did not. The experiment at 212°C levels off at a very low relative pressure increase.

In view of the complexity of these results we have, for the present, not pursued this line of endeavor.

3. Thermal Decomposition Experiments with HDP-Copper Chromite Mixtures

Differential thermal analysis experiments with HDP copper chromite mixtures containing 5% and 10% copper chromite showed exotherms at 140°C and 130°C respectively. Experiments with the mixture containing 10% catalyst were performed at 135°C and 142°C but reaction was very slow--i.e., a few percent reaction in an hour.

Experiments were then performed at 291°C with mixtures containing 5 and 10% catalyst. In each case explosion occurred after about forty-five seconds.

4. Product Examination of a Quenched Deflagration

A strand of HDP was ignited with a hot wire at an ambient

pressure of 21 atm of nitrogen. After deflagration had started, the pressure was released and deflagration ceased. Examination of the residue of the strand by infrared spectroscopy showed that hydrazine diperchlorate and ammonium perchlorate were present. This is strong evidence that the processes occurring during deflagration are the same as those occurring during thermal decomposition.

C. Measurements of the Rate of Deflagration of HDP

We have performed further experiments with HDP in an effort to obtain consistent deflagration rate data. The most recent results have been obtained, for the most part, with a single batch of HDP. They are tabulated in Table IV.

Before considering the total results it is necessary to point out certain features of the data. It will be noted that the tabulated data include deflagration measurements at pressures of six atmospheres. In previous experiments of this type (2) we have been unable to obtain steady deflagration below about 21 atm. In the course of attempting to quench deflagrating strands of HDP by rapid lowering of the ambient pressure, we observed that deflagration continued slowly but steadily at the lowered pressures. A re-examination of the pressure regime between 1 and 15 atmospheres has shown that reproducible deflagration can be obtained down to a pressure of six atmospheres. The mode of ignition is an important factor here. When ignition is attempted by igniting a layer of plastic propellant on top of the strand, we have found that, at low pressures, the propellant layer frequently burns completely, without igniting the HDP. A steady application of a hot wire yielded more reproducible results.

The pressure range of deflagration for HDP that we have examined to date is from 6 to 131 atmospheres. In Figures 2 and 3 the results are plotted as the linear and mass deflagration rates. Points for ammonium perchlorate are included in Figure 2 for comparison (9).

The curves are fairly parallel. The linear deflagration rate data for HDP are plotted on log-log scales in Figure 4. The points are fairly linear from 6 atmospheres to about 70 atmospheres and fall below the line at higher pressures. This too is similar to the case

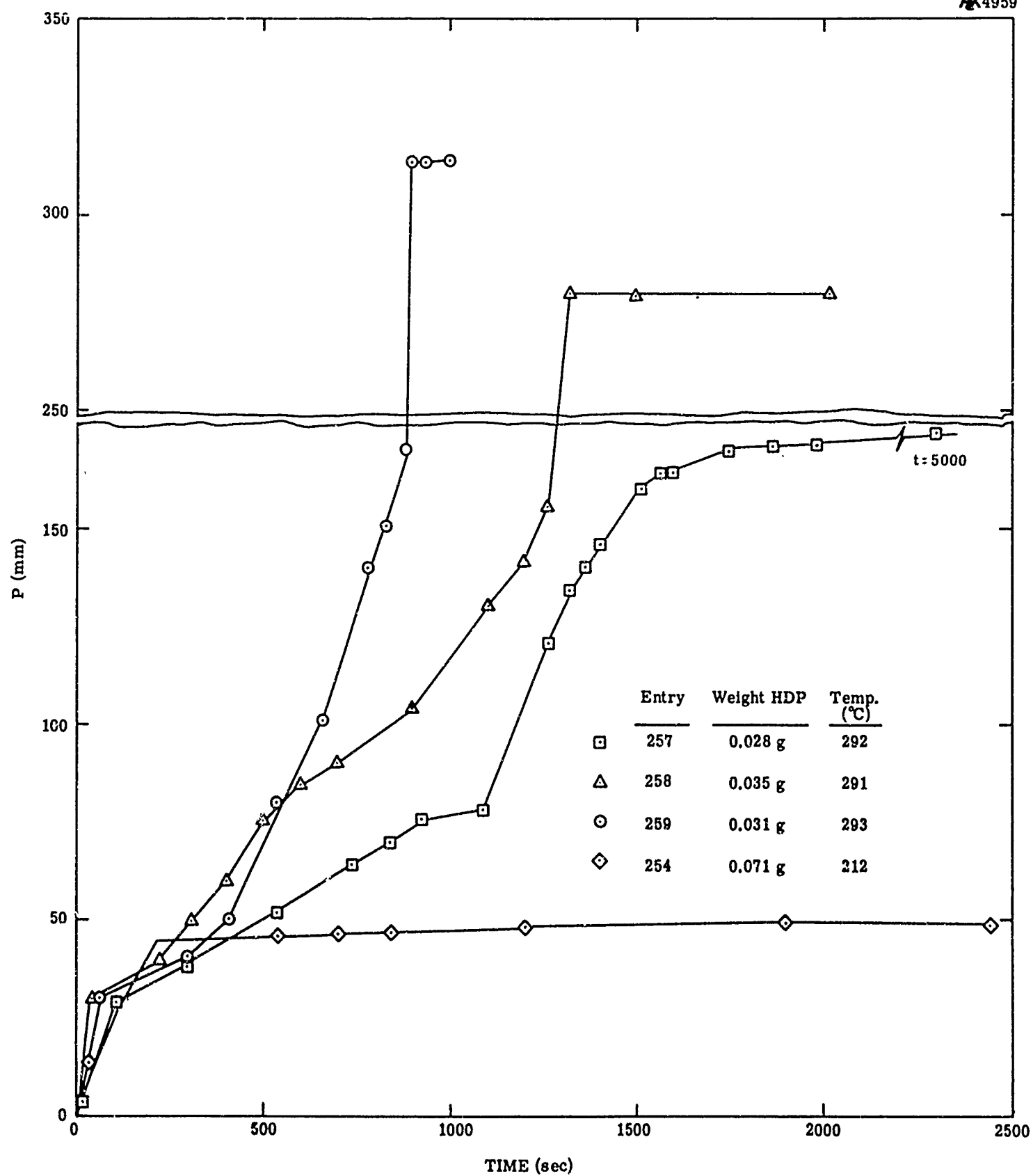


Figure 1. The Rate of Thermal Decomposition of Hydrazine Dperchlorate.

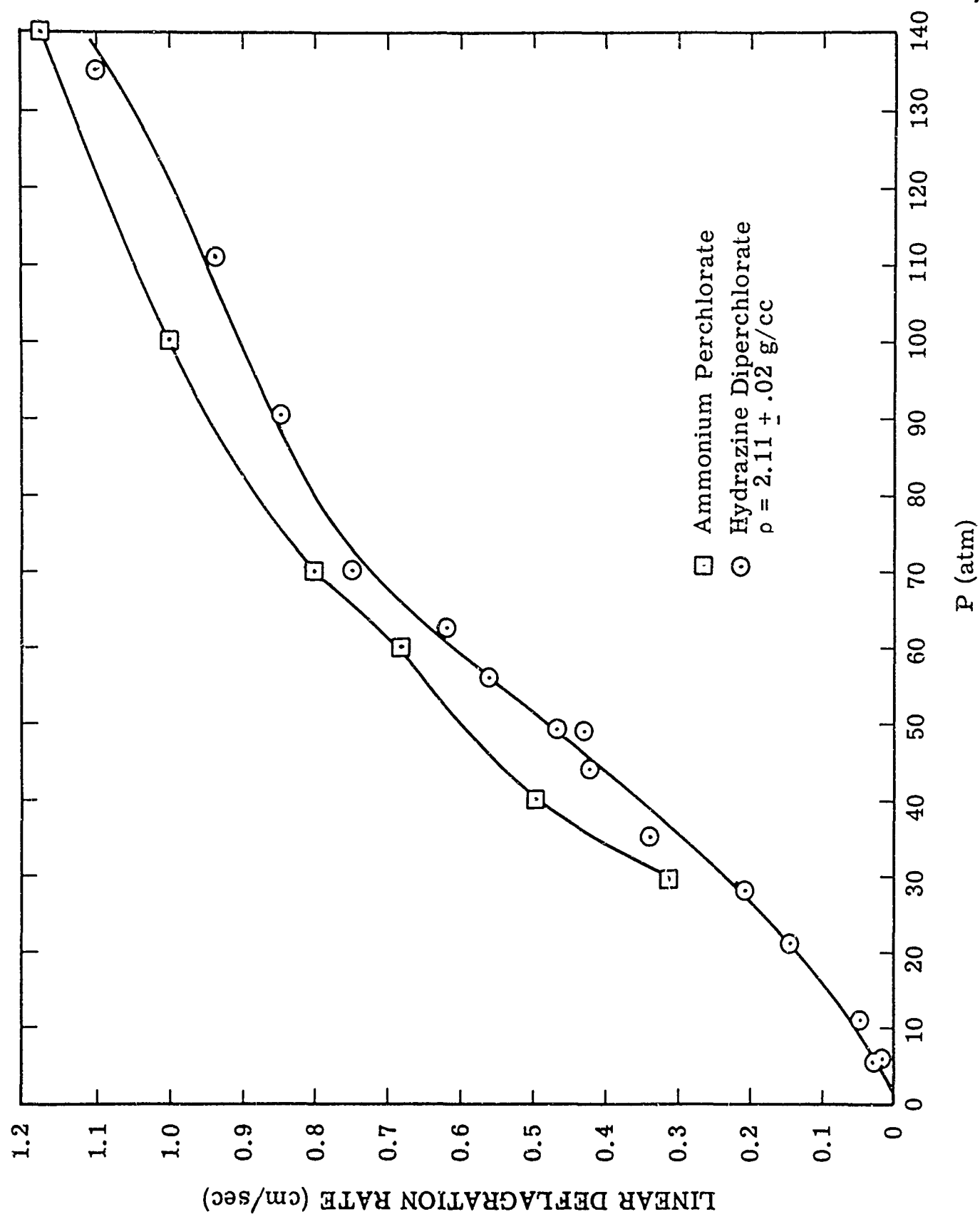
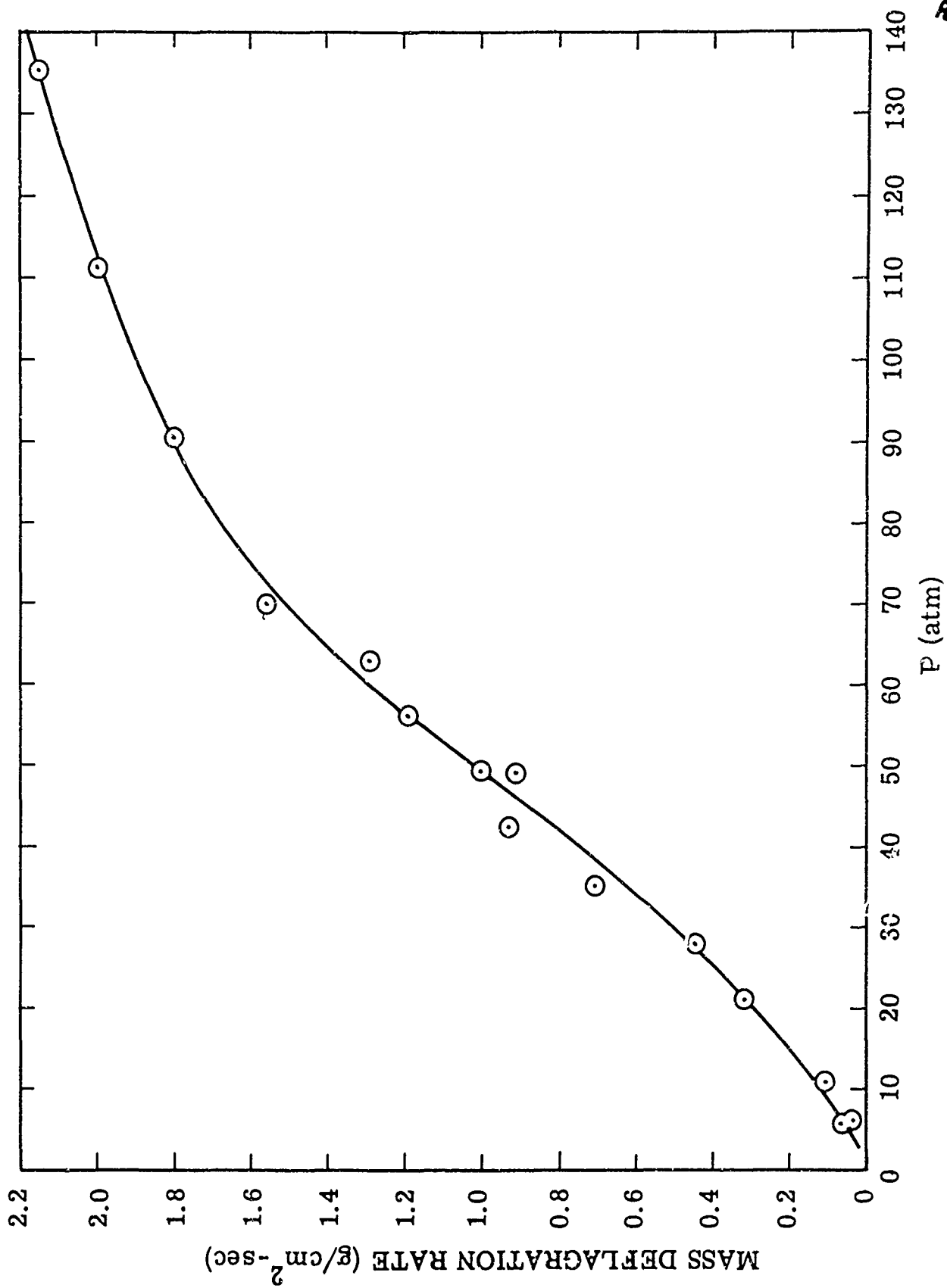


Figure 2. Linear Deflagration Rate of Hydrazine Diperchlorate and Ammonium Perchlorate as a Function of Pressure.



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Figure 3. Mass Deflagration Rate of Hydrazine Diperchlorate as a Function of Pressure.

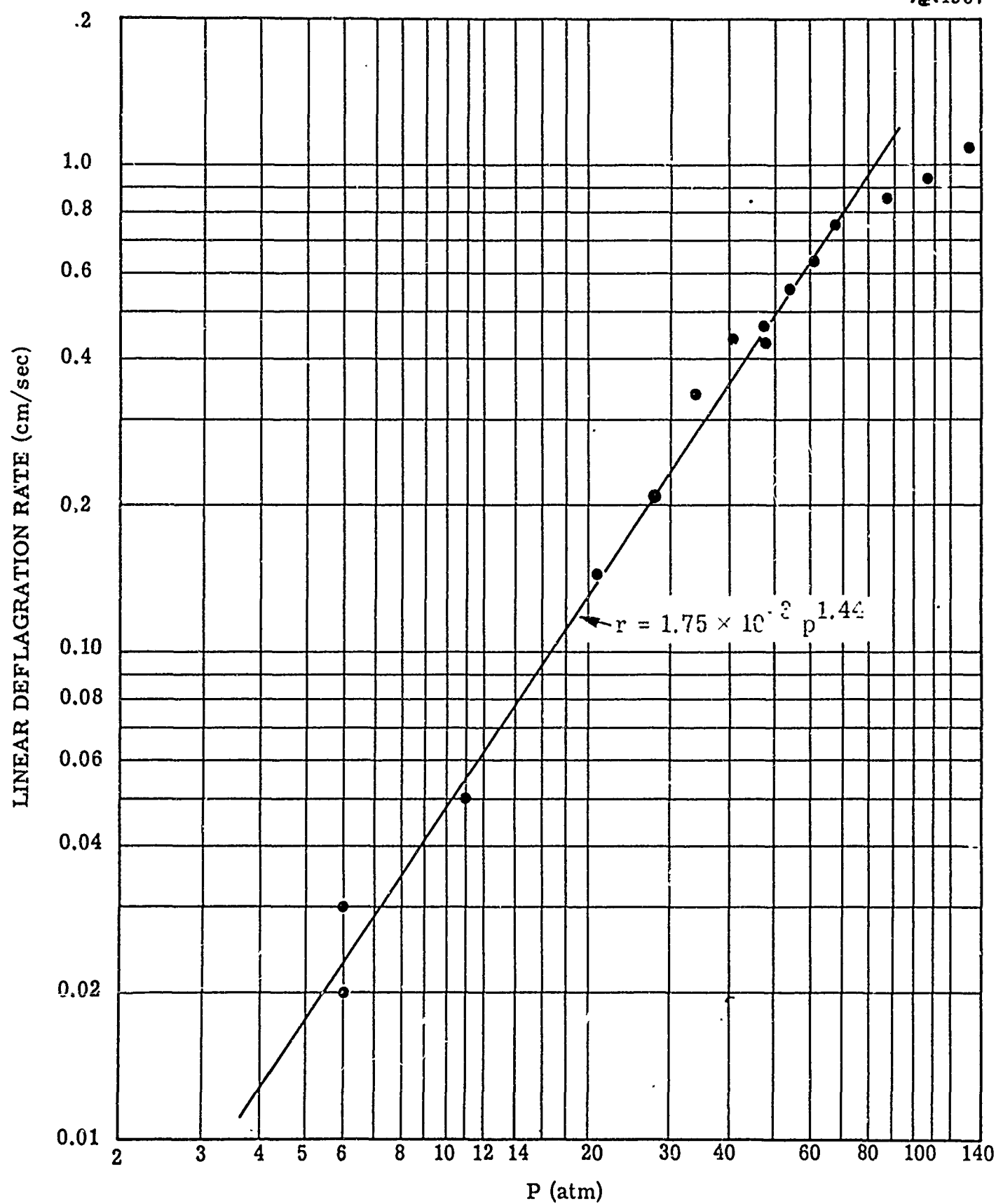


Figure 4. Deflagration Rate Versus Pressure for HDP, Log-Log Plot.

TABLE IV

Deflagration Rate Measurements with
Hydrazine Diperchlorate
($\rho = 2.11 \pm 0.02$ g/cc)

Entry	P (atm)*	Linear Rate cm/sec
287	6.0	0.03
287	6.0	0.02
287	11.0	0.05
279	21.0	0.145
285	27.7	0.21
278	34.3-34.6	0.34
278	41.0-41.3	0.44
278	47.7-48.3	0.47
285	47.7-48.0	0.43
278	54.3-55.0	0.56
278	61.0-61.7	0.62
279	67.7-68.7	0.75
286	87.7-89.0	0.85
288	107.5-108.9	0.94
288	131.1-132.0	1.10

* The intervals indicate pressure range during deflagration

for ammonium perchlorate (9). The linear portion of Figure 4 has a slope of 1.44 and the linear deflagration rate for this region, i.e., 6 to 70 atmospheres may be expressed by $r = 1.75 \times 10^{-3} P^{1.44}$, where the units of r and P are cm/sec and atmospheres respectively. For ammonium perchlorate the estimated slope for the corresponding curve was about unity.

IV. PLANS FOR THE FUTURE

During the next period we plan to make more measurements of the flame temperature above deflagrating hydrazine dperchlorate both at 21 atm and at higher pressures. If the results confirm that the theoretical flame temperature is not attained, the products of deflagration will be analyzed to establish their nature.

Thermal profiles through the subsurface portion of strands deflagrating at various pressures should be of interest. It is quite possible that condensed phase reactions play a role in the deflagration and that the importance of the contribution is a function of pressure. Thermal profile measurements should be informative here.

We have observed temperature and catalyst concentration regimes where the thermal decomposition of HDP-catalyst has been very slow or explosive. We plan to explore the variation of catalyst content and temperature to see if a regime can be found where the thermal decomposition proceeds at a measurable rate. Kinetics and product analysis experiments would then be in order.

We plan to extend our deflagration rate measurements to the highest pressure attainable in our bomb, i.e., to 300 atmospheres.

V. REFERENCES

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